Structure of the orthorhombic γ-phase and phase transitions of $Ca(BD_4)_2$

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(Dated: August 21, 2009)

I. SUPPORTING INFORMATION

A. Data collection

For the synchrotron radiation X-ray powder diffraction (SR-XPD) data collection, the samples were filled into 1.0 mm diameter glass capillaries. For the neutron powder diffraction (NPD) data collection, due to the high neutron absorption of natural boron, the powder of $Ca(BD_4)_2$ was filled into a sealed double walled vanadium cylinder of 9 mm outer diameter, 7 mm inner diameter and 50 mm length. The absorption correction coefficient of the sample $\mu R = 0.296$ was determined by transmission measurements.

B. Rietveld refinement of the final structural model in *Pbca* symmetry

X-ray form factors and neutron scattering lengths from the FullProf library were used. A weight of 0.5 for the NPD and SR-XPD data was given in the combined refinement. The 107 free parameters (including additional phases) of the final refinement of the γ-phase are divided as follows: Three unit cell parameters, 33 atomic coordinates, three isotropic displacement parameters were refined (all D atoms are constrained to have the same displacement parameters, the same holds for B atoms). The additional phases were included into the refinement to account for the $Ca(BD_4)_2$ β-phase, the $Ca(BD_4)_2$ α-phase, and CaD_2 traces. A fifth phase (vanadium) was included into the refinement only for the NPD data to take into account the diffraction from the sample holder. For these four phases, a total of 40 structural parameters (unit cell, atomic coordinates, displacement parameters) were refined. From quantitative phase analysis the respective refined weight fractions of the phases present in the sample are 48% for the γ-phase, 31% for the β-phase, 16% for the α-phase, and 5% for the CaD_2. Thomson-Cox-Hastings modified pseudo-Voigt profile function was used to model the peak shape for both the SR-XPD and NPD diffraction patterns. For the SR-XPD data, the instrumental profile parameters (U and V) were refined by the fitting of a data measured for a $Na_2Ca_3Al_2F_{14}$ (NAC) standard. The sample profile parameters were refined by a profile matching of the $Ca(BD_4)_2$ SR-XPD data. The instrumental and sample profile parameters for the SR-XPD data were kept fixed at these values for the final refinement. For the NPD data profile, four profile parameters were used in the final refinement. In addition, two zero shift parameters, the neutron wavelength and 9 scale factors were refined. The

background was modelled by a Fourier-cosine series with 12 refined coefficients for the NPD data and by an interpolation between 42 fixed points for the SR-XPD data.

C. Deviation of the low-symmetry models from *Pbca* symmetry

All the refined structural candidates were found to give very similar quality of fit for both neutron and X-ray pattern (see Table I). The refined structural models of the space groups $P2_12_12_1$ and $Pca2_1$ were found to be qualitatively very similar to the higher symmetry structural model with space group *Pbca* (see Figure 1), suggesting that the symmetry operations of the space group *Pbca* are de facto embedded in the four structural models refined in lower symmetry (the space groups $P2_12_12_1$ and $Pca2_1$ are indeed subgroups of the space group *Pbca*). From Figure 1, it is clear that the refined shapes and orientations of the BD_4 groups of the restrained structural models with space groups $P2_12_12_1$ and $Pca2_1$ closely match the higher symmetry structural model with space group *Pbca*. Considering that $P2_12_12_1$ and $Pca2_1$ are subgroups of the space group *Pbca*, it follows from the similarity of the structural models that the symmetry operations of the space group *Pbca* are approximately present also in the four refined lower symmetry structural models. This is further reflected in SR-XPD reflections intensities of the low symmetry space group candidates where reflections not fulfilling the reflections conditions of the *Pbca* symmetry have a negligibly little intensities. One has to keep in mind, however that in the X-ray data, the contribution of deuterium atoms to the reflection intensities is small compared to the heavier atoms, thus the deductions based on reflection conditions essentially reflect the Ca and B network symmetry. This was quantitatively checked and confirmed using the symmetry determination capability of the software Superflip.

D. Calculations with Superflip

In the present case, the tested density was the electron density generated by placing neutral atoms at the atomic positions corresponding to the refined models. The scattering factor of deuterium was replaced by the scattering factor of carbon in order to increase the relative weight of the deuterium atomic positions in the symmetry test with respect to the heavier boron and calcium atoms. Without the scattering factor substitution of the D

atoms with C atoms, the agreement factor would be smaller than 2%, but such a test reflects mainly the symmetry of the Ca and B network, which clearly obeys the *Pbca* symmetry. This information is available free of charge via the Internet at http://pubs.acs.org.

Tables and Figures for Supporting information

TABLE I: Summary of the Rietveld refinement results of the structural model candidates: Agreement factors and B-D interatomic distances of independent BD_4 tetrahedra in the unit cell. The orthogonal lengths l_1=13.0584(8) Å, l_2=8.3881(4) Å, l_3=7.5107(4) Å of the orthorhombic unit cell are attributed to the unit cell vectors (a;b;c), according to different projections of the space groups.

Space Group	Rwp* NPD/SR-XPD	χ^2 NPD/SR-XPD	$B-D$ (Å)
Pbca (a=l_1; b=l_2; c=l_3)	1.09/10.3	4.83/3.54	1.06(3)-1.24(3)
			1.17(3)-1.33(3)
$Pca2_1$ (a=l_1; b=l_3; c=l_2)	1.00/10.3	4.05/3.52	1.08(7)-1.46(7)
			1.02(8)-1.36(8)
			1.14(7)-1.71(8)
			1.08(8)-1.30(7)
$Pca2_1$ (a=l_3; b=l_2; c=l_1)	1.03/10.3	4.36/3.52	1.10(6)-1.35(7)
			1.03(8)-1.35(8)
			1.06(8)-1.30(8)
			1.05(7)-1.38(9)
$Pca2_1$ (a=l_2; b=l_1; c=l_3)	1.02/10.2	4.26/3.50	1.10(8)-1.30(8)
			0.94(7)-1.21(8)
			0.98(8)-1.42(9)
			1.09(8)-1.35(7)
$P2_12_12_1$ (a=l_1; b=l_2; c=l_3)	1.02/10.3	4.29/3.52	1.04(9)-1.35(8)
			0.91(7)-1.26(8)
			1.20(8)-1.59(7)
			1.13(8)-1.40(8)

* Weighted profile factor.

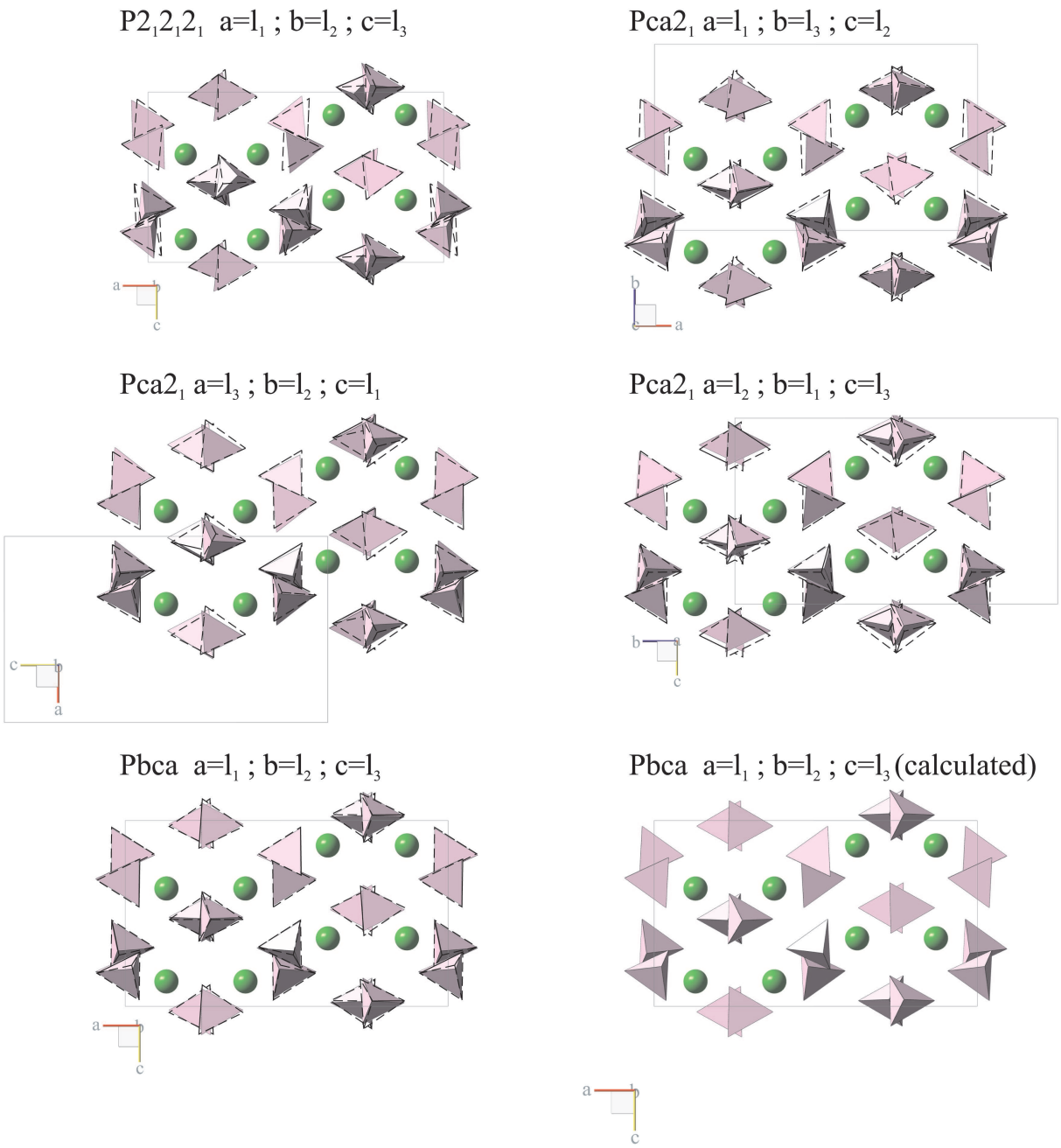

FIG. 1: Refined $Ca(BD_4)_2$ γ-phase structural models, and calculated structure in *Pbca* symmetry viewed in the plane (010). To emphasize the similarity of the Ca-B networks for the different structures, only the BD_4 shape is drawn and the atoms are not always represented in the conventional unit cell (drawn by black frames). Edges of the BD_4 refined with anti-bump soft restraints are drawn with dashed lines.

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